



Origin of heat-induced structural changes in dissolved organic matter

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HIGHLIGHTS

- Reactivity of DOM strongly depends on its concentration.
- Different parts of total compressibility play role at different concentrations.
- Progressive dilution causes weakening of the aggregate's stability.
- H-bonds and aromaticity are responsible for main phase transitions in diluted DOM.
- DOM exhibits structural hysteresis under fluctuating temperature.

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ABSTRACT

Humic substances play an important role in many environmental processes such as sequestration and transport of hydrophobic compounds. The supramolecular character of humic substances imparts high flexibility of the aggregates associated with their variable reactivity under different conditions. In this study, heat-induced transitions and character of the hydration shell of sodium salts of humic and fulvic acids originating from various sources were investigated using ultrasonic velocimetry in the temperature interval from 5 to 90 °C. Results clearly showed differences in stability and characteristics of the hydrated states at concentrations above and below 1 g L⁻¹ with the exception of Pahokee peat fulvic acids. It has been concluded that predominantly the relaxation part of the adiabatic compressibility plays an important role below 1 g L⁻¹ in contrast to both relaxation and intrinsic parts of the compressibility being important at higher concentrations. Dilution brought several temperature induced transitions which were investigated with respect to composition of all investigated humic substances. Correlation analysis revealed that the transition around 17 °C is associated with disruption of H-interactions whereas the transition around 42 °C depends on the aromaticity. Comparison of cooling and heating records revealed hysteresis in the structural relaxation resembling the behavior of physically stabilized hydrogels. Results indicated a difference in the conformation and therefore reactivity of dissolved humic substances in the dependence on temperature and thermal history. It has been hypothesized that this may play an important role in the transport and sequestration of hydrophobic pollutants by dissolved organic matter.

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1. Introduction

Humic substances are a versatile and complex heterogeneous mixture of molecules with pronounced roles in terrestrial and aquatic environments (Stevenson, 1994). Traditionally they are divided into three categories according to their solubility: fully soluble fulvic acids, humic acids soluble in alkaline solutions, and insoluble humin (Zsolnay, 2003). Various chemical compounds

originating from plant tissue and residues of microbial biomass and animal bodies can be identified in their primary structure. Those are mainly constituents derived from lignins, cellulose, proteins, cutins and suberins (Sutton and Sposito, 2005).

Nowadays, lacking a consensus on the physical arrangement of their molecules, humic substances are considered to be either macromolecules (Swift, 1999) or supramolecular associations of relatively small molecules (Piccolo, 2001), or combination of both (Schaumann, 2006). Some of recent results achieved by various techniques such as high performance size exclusion chromatography (Piccolo et al., 1996; Piccolo, 2001), nuclear magnetic resonance (Smejkalova and Piccolo, 2008), electrospray ionization mass spectrometry (Piccolo and Spiteller, 2003), and electron spin

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resonance (Ferreira et al., 2001) favor the supramolecular concept. Accordingly, humic substances can be visualized as molecules of molecular weights up to 1200 Da (Piccolo and Spiteller, 2003) forming large aggregates held together by weak dispersive forces such as van der Waals, π - π , CH- π interactions, and H-bonds (Piccolo, 2001).

Humic substances represent a stable part of dissolved organic matter (DOM) which plays a role in many environmental processes and is thought to be a sensitive indicator of their fluctuations (Bolan et al., 2011). Therefore the behavior of humic substances in diluted solutions is of great interest. Based on surface tension measurements (Hayase and Tsubota, 1983; Guetzloff and Rice, 1994), NMR Diffusion Ordered Spectroscopy (Simpson, 2002; Smejkalova and Piccolo, 2008), and conductivity and phenanthrene solubility measurements (Quagliotto et al., 2006) some authors concluded that dissolved humic substances form micelles at critical micelle concentration similarly as classical surfactants do. The major forces that govern self-assembly of the amphiphiles into well-defined structures such as micelles, bilayers or three-dimensional networks derive from the hydrophobic effect; their stability depends on the hydrophobic attraction at the hydrocarbon-water interface and the competing steric repulsion of hydrophilic head groups (Israelachvili, 2011). Dissolved humic substances reduce the surface tension and form hydrophobic domains which are able to solubilize hydrophobic compounds (Ferreira et al., 2001), but they do not always behave in the same way as classical surfactants (Kucerik et al., 2007). That is demonstrated by a decrease in the amount of solubilized hydrophobic compounds with increasing humic acids concentration (Alawi et al., 1995; Lassen and Carlsen, 1997), which is in contrast to behavior of classical amphiphilic surfactants solubilizing hydrophobic molecules mostly around and above a critical micelle concentration (CMC). For very hydrophobic compounds, dissolved humic acids show a significant sorption effect already at concentrations as low as 10 mg L^{-1} (Kopinke et al., 2001). Further Terashima et al. (2004) reported the study dealing with solubilization of *p*-dichlorobenzene by dissolved humic acids at pH 4 and 7. Recalculation of ratio between *p*-dichlorobenzene and humic acids concentration gives the largest values for lower concentrations of humic acids (Terashima et al., 2004). The ability of dissolved organic matter (DOM) to solubilize hydrophobic compounds at low concentrations has already been interpreted by Wershaw (1999) by either partition of hydrophobic molecules into interiors of aggregates of amphiphilic molecules at concentrations lower than CMC (premicellar aggregates), or association of hydrophobic molecules with the non-polar parts of unassociated amphiphilic molecules. Indeed the existence of the premicellar or pseudomicellar aggregates was confirmed by Engebretson and von Wandruszka (1997); Yates et al. (1997); von Wandruszka (1998). Recently these observations have been confirmed by ultrasonic velocimetry which shows that the aggregates in dissolved lignite humic acids or humates (Kucerik et al., 2007) and fulvic acids (Drastík et al., 2009) were still present at concentrations as low as 10^{-3} g L^{-1} . This technique was later combined with surface tension measurement (Ctvrtnickova et al., 2011) which revealed that reformation of the aggregates in bulk solution took only several minutes, whereas reaggregation processes occurring at the air/solution interface took several hours. This observation was attributed to slower reorientation kinetics of molecules adsorbed in the interface which can be a consequence of changes in the hydrodynamic characteristics of water motion at the water/DOM interface (Ramus et al., 2012).

Due to the polyelectrolyte character, the physical structure and aggregation of dissolved humic substances is a function of their composition and concentration, pH, type of electrolyte and ionic strength in the solution, and temperature (Pinheiro et al., 1996; Tombacz, 1999; Terashima et al., 2004).

Application of sound waves as a probe is a non-destructive approach based on characterization of low energy ultrasonic waves at one frequency (velocimetry) or at several frequencies (spectroscopy). A sinusoidal oscillating pressure (stress) produced by a piezo crystal causes oscillation between compression and decompression (mechanical deformation) of a sample and measures the attractive and repulsive forces within molecules (an analogy to rheometry). The measured parameters are the attenuation and velocity of an ultrasonic wave propagating through the analyzed sample. As reported recently, DOM at relevant environmental concentrations can be analyzed mainly by measurement of the ultrasonic velocity (Kucerik et al., 2007). It was also demonstrated that velocimetry can be used for analysis of dissolved humic substances over a wide concentration range, from 10^{-3} to tens of g L^{-1} (Kucerik et al., 2009).

The speed of sound in liquids can be expressed as:

$$U^2 = \frac{1}{\rho \beta_S} \quad (1)$$

where U stands for sound velocity, ρ for density, and β_S for adiabatic compressibility. The adiabatic compressibility β_S is the fractional decrease of volume per unit increase in pressure, without any heat flow in or out. In DOM, similarly to the systems of dissolved proteins, the adiabatic compressibility β_S is the sum of three components: (i) the intrinsic adiabatic compressibility of hydration shell, K_h , (ii) the intrinsic compressibility of DOM, K_M , and (iii) relaxation contribution, K_r . The most important factor for small molecules in solution is usually the contribution of K_h (Buckin, 1988). In the case of larger molecules such as globular proteins, the K_M can reach the same order as K_h , and K_r is usually less than 5–10% of the total compressibility (Sarvazyan, 1991). Based on the above mentioned findings about the physical structure of DOM, it can be assumed that the imperfect packing of individual molecules in DOM and the fluctuating dynamic structure are the reason for a high intrinsic compressibility K_M as well as the relaxation contribution K_r .

Both density and adiabatic compressibility in Eq. (1) are influenced by temperature. In water the impact of temperature is enormous and, unlike in other liquids, non-linear. At low temperatures, both compressibility and density are high, which decreases the sound velocity (Eq. (1)). As temperature increases, compressibility drops and goes through a minimum whereas the density goes through a maximum and then drops. Combination of these two properties leads to a maximum sound velocity at 74 °C. As a result, the high resolution measurement of the ultrasonic velocity provides a possibility to investigate the molecular organization and intermolecular interactions. Many successful applications of velocimetry and ultrasonic spectroscopy in medicine, biochemistry (Buckin et al., 1989), food industry (Hodate et al., 1997), and studies of various types of materials and processes (Resa and Buckin, 2011) have been reported. Detailed description of mechanisms of the ultrasonic velocimetry can be found in the paper by Sarvazyan (1991).

The purpose of this work is to extend the previous research carried out using ultrasonic velocimetry (Kucerik et al., 2009) and to verify if the findings obtained for lignite humic acids can be generalized and applied to dissolved humic (HAs) and fulvic acids (FAs) of various origin. The previous study showed that sodium humates form aggregates even at concentrations around 10^{-3} g L^{-1} and their fractal dimension depends on the concentration and type of counter ion (Drastík et al., 2009). Heating of humate solutions revealed that character of the aggregates depends strongly on concentration (Kucerik et al., 2009). Further, several reversible transitions in the humate structure were observed in diluted solutions. However, it is still not known if those transitions are characteristic only for lignite humates or if it is a

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